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(71) Applicant (*for all designated States except US*): EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): AGARWAL, Pawan, Kumar [US/BE]; Rue Crolle 32, B-1328 Ohain (BE).

(74) Agents: VELDHUIZEN, Albert, Dirk, Willem et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).

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(54) Title: ELASTIC POLYETHYLENE COMPOSITIONS

(57) Abstract

Polyethylene compositions exhibiting varying degrees of crystalline-amorphous regions are disclosed. Such materials are obtained by combining high molecular weight homopolymer polyethylene chains (M_w greater than or equal to about 1.5×10^6) with conventional polyethylene polymers, such as low density, linear low density, and high density. Blend compositions in accordance with the invention exhibit non-linear elongational characteristics, due to enhanced elasticity, and are particularly suitable for film blowing and associated applications such as oriented and non-oriented packaging films and molding applications.

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ELASTIC POLYETHYLENE COMPOSITIONS

Technical Field

This invention relates to polyethylene blend compositions comprising one or more of conventional polyethylene polymers or copolymers, with additionally, high molecular weight polyethylene (M_w greater than 1.5×10^6), the blend compositions exhibiting enhanced elastic properties.

Background of the Invention

The level of elasticity in polyethylene films is a critical property for both of film production speed and coating speed. For example, during the film blowing operation conventionally used, the bubble stability is controlled by the elasticity of the (partially melted) film as it is being stretched, cooled and picked up by the chill and take-up rolls. Additionally, the elastic properties are important in molding applications for both of processing and composition final properties.

Certain polyethylene blends comprising both of high M_w polyethylene and one or more conventional polyethylene polymers or copolymers are known in the patent art, typically for injection molding compositions. This is because ultrahigh molecular weight polyethylenes are known to have exceptional abrasion and impact resistance.

An early description of molded polyethylene compositions, JP-A-59-232164, disclosed the use of A) 50 - 15 parts superhigh molecular weight polyethylene, having an intrinsic viscosity [η] in decalin at 135°C of at least 5 dl/g and a density of 0.930 g/cm^3 or more, and b) 50 - 85 parts high-density polyethylene, having a density of 0.950 or more and and MFR of 0.1-500 g/10min, for the purpose of providing a latent-heat-type thermal energy material said to show excellent shape retention when being melted. The methods of production are said to include both i) mixing

with melt-kneading and extrusion into pellets, strands, films, sheets, or nets and b) mixing with forming into strands or sheets by an injection or compression process.

US-A-4 792 588 describes ethylene compositions said to have excellent melt moldability comprising 20 - 95 wt.% ultrahigh-molecular-weight polyethylene with molecular weight of at least 1,650,000 and 80 - 5 wt.% of a low-molecular-weight to high molecular-weight polyethylene of about 1500 to about 360,000. The compositions are produced by a multi-stage, multi-reactor process. The mechanical properties of high impact resistance or strength and tensile strength of the ultrahigh-molecular-weight polyethylene is said to be retained. Molded products are described, including molded sheets of 2 - 5 mm. thickness. High speed-formed, thin films of a thickness up to 6 microns and mouldings from compositions comprising 85 - 50 wt.% A) polyethylene compositions consisting of a broad ratio of low mol. wt. PE (mol. wt. 5,000 - 50,000) and high mol. wt. PE (mol. wt. 100,000 - 1,500,000) and, 15 - 50 wt.% B) polyethylene having mol. wt. 90,000 - 500,000 are described in an Abstract of JP-A-0 026 049.

Enhanced elasticity properties are not directly addressed in the above published documents, nor are morphological characteristics described that would lead directly to development of the improved elasticity compositions that are the subject of the claimed invention.

Invention Disclosure

It has been surprisingly found that by combining high weight-average molecular weight polyethylene (M_w greater than about 1.5 x 10^6) with conventional polyethylene polymers, polyethylene compositions exhibiting varying degrees of crystalline-amorphous regions can be prepared.

These blend compositions exhibit non-linear elongational characteristics, due to enhanced elasticity, and accordingly are particularly suitable for film blowing and associated applications such as oriented and non-oriented packaging films.

Best Mode and Examples of the Invention

The high weight-average molecular-weight polyethylene (HMWPE) of the invention are those polyethylenes which have a M_w greater than or equal to about 1.5 x 10^6. Included are the ultrahigh molecular-weight ("UHMW") polyethylenes defined by the ASTM as those linear polyethylenes which have a relative viscosity of 2.3 or greater, at a solution concentration of 0.05%, at 135°C., in decahydronaphthalene. Typically HDPE has molecular weights in the range of 100,000 to 200,000, and HMW HDPE has molecular weights in the range of 300,000 to 500,000 (see below). The high molecular weight homopolymer polyethylene of the invention is substantially higher in M_w, and will typically be on the order of 1.5 x 10^6, or higher. Commercial grades are available from 3 x 10^6 to 6 x 10^6, normally in powder form. Typically the HMWPE can be prepared by any of radical polymerization of ethylene under high pressure, coordination polymerization of ethylene, and polymerization of ethylene with supported metal-oxide catalysts, preferably and, generally commercially, by means of the latter two. Additional background information on UHMW appears in the technical literature, see e.g., Ency. of Poly. Sci. and Eng., vol. 6, pp. 490-494 and 383-490 (J. Wiley & Sons, 1986), and Textbook of Polymer Science (3d ed.), F.W. Billmeyer, Jr., Pages 366-367 (J. Wiley & Sons, 1984).

The term "conventional polyethylene polymers" includes one or more of ultralow-density ("ULDPE"), very low density ("VLDPE"), low density ("LDPE"), linear low density ("LLDPE"), high density ("HDPE"), and high molecular weight high-density ("HMW HDPE") as those terms are understood in the art, see e.g., Ency. of Poly. Sci. and Eng., above, and Modern Plastics Encyclopedia (1988). Both homopolymers and copolymers are included, the polyethylene copolymers typically are those of ethylene with at least one alphaolefin having at least three carbon atoms, e.g., propylene, 1-butene, 1-hexene, 1-octene, etc. Additionally these blends will encompass any of the polyethylene polymers and blends emerging from new technologies relating to metallocene coordination catalysis, such as those exemplified in PCT-A-WO 90/03414. The disclosures addressing polyolefins and blends thereof in U.S. application number U.S. application Ser. No. 252,094 filed 30 September 1988 and U.S. application Ser. No. 07/817,701 filed 7 January 1992 are incorporated by reference for purposes of U.S. patent practice.

Typically the invention blends comprise from 0.1 to 40 wt.% based upon the total polymer weight, more particularly 2 to less than 40 wt.% of the HMWPE of the invention. The complement will comprise the conventional polyethylene polymers or copolymers. Additionally, as with other polyolefin blends, additives such as reinforcing fillers, pigments or colorants, UV stabilizers, antioxidants, anti-block or slip agents, etc., can be provided in conventional amounts in accordance with conventional methods to achieve specifically desired end properties. Such additives can be added in any order convenient prior to or during melt blending of the blends.

Blends of the invention are prepared by blending the described components in the desired proportions using either conventional solution or melt processing techniques

and apparatus for example, solution-melt extruders, Banbury mixers, single or multiple screw extruders and the like. The ultra high molecular weight polyethylene by itself is known to be be difficult to process via conventional polyethylene processing techniques. However it can be successfully processed by a newly developed but well established technique called gel spinning. Exceptionally high strength highly extended polyethylene fibers are produced by this technique. Similarly, they are processed in the solid-state by sintering and extrusion, a technique analogous to injection extrusion processes used for manufacturing pipes or plastics or ceramics. The techniques are known to those familiar with field of polyolefin processing. Any such technique could be used for preparing the said composition disclosed herein. Alternatively, blends may be made by direct polymerization, using, for example, two or more catalysts in a single reactor or one or more catalysts in parallel or series reactors; where the catalysts, monomer feeds, and reactor conditions are provided that are suitable for the preparation of polymer components meeting the invention description. Such direct polymerization blends are well-known in the polyolefin art, see e.g., US-A-4 792 588.

Though not intended as a limitation on the invention as described, it is believed that there is synergistic formation of morphology having crystallite structure and associated amorphous regions such that surprisingly high elongations are achieved. Measurement by DSC (differential scanning calorimetry) showed that blends of conventional polyethylene polymer (LD-180 of Exxon Chemcal Belgium, M.I. 2.0 (190°C., 2.16 kg)) and ultra-high molecular weight polyethylene (GUR-412 of Hoechst Aktiengesellschaft, DE; weight-average M.W. 2 x 10^6), exhibited not only phases of the two individual components, but also a third phase having a distinct melting temperature Tm. Thus, for example, a binary blend of these polymers in the ratio of

90/10 showed three melting endotherms at 107, 124 and 133°C indicating three different kinds of crystalline lamellae populations. This is contrary to the published literature, see for example J. Polym. Sci., Phys. Ed., 25, 89 (1987) and Polymer, 32, 426 (1991). Here it is clearly mentioned that the basic crystalline structure of either component does not change during mixing, and upon cooling the melt of blend of such polymers, the respective crystalline structure of the components is retained. These published works clearly mention that only in certain cases, for example in blends of HDPE and LLDPE both having nominal molecular weights in the range of 50-100,000, does co-crystallization take place. The presently discovered novel behavior of the blend demonstrated the existence of at least three types of crystalline phase structures in the blends of said materials composition of blends of LDPE and UHMWPE.

The mechanisms by which the elongation of conventional polyethylene increases upon the addition of very long molecular weight polyethylene chains was not readily apparent. However the phenomenon is obtained in cases where the ratio of the molecular weight of conventional and high molecular weight polyethylene ("M_C/M_H") is preferably less than 1; more preferably less than 0.1 and most preferably less than 0.01. In other words, the M_C/M_H, where M_H is the molecular weight of UHMWPE and M_C is the conventional polyethylene is such that $M_H/M_C > 1$; more preferably $M_H/M_C > 10$ and most preferably > 25. Note M_H in examples 2-10 below is about 2,000,000 and M_C is 60,000. Thus M_H/M_C is about 35.

Typical industrial applications for the blends of the invention are the field of polyolefin films, especially in thin guage films where strength and elasticity are important to fast processlng. The blends exhibit excellent bubble stability and fast drawdowns during film blowing

operations. All of unoriented and singly, or doubly, oriented packaging films for such end-use as food, health care or consumer articles enclosures can be prepared from the blends of this invention in accordance with conventional knowledge in the field. Additionally the invention blends are suitable for injection molding purposes. Items that are normally injection molded such as mechanical goods, household utensils, toys, etc. which use polyethylenes as such or polyethylene compositions incorporating polypropylene and/or ethylene-propylene copolymers, can be made from the disclosed compositions described in this invention.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect.

<u>Examples 1 to 11</u> - Invention blend compositions of a commercial high density polyethylene (HDPE - 6950 YN, a product of Exxon Chemical Co., U.S.A.) and a commercial high density and ultrahigh molecular weight polyethylene (GUR-412 - Lot CM 331584, Hoechst Aktiengesellschaft, DE) were made. The weight-average molecular weight of the former as determined by GPC (gel permeation chromatography) was 62,000 and its Mw/Mn ratio about 4.6. Its melting temperature determined from DSC @ 10°C/min was found to be 137.4°C and room temperature density as determined by the standard ASTM D-1505 (equivalent DIN-53479D Iso-R-1183D) procedure was found to be 0.96 (g/cm^3). Similarly, the weight-average molecular weight of UHMWPE was about 2,000,000 and its Mw/Mn ratio greater than 5.0. Its melting temperature and density values were 133.5 and 0.93 (g/cm^3), respectively. The blend compositions were made by dissolving the appropriate quantities of the material in

hot xylene at 130°C for at least 2 hours with constant mechanical stirring or occasional hand shaking of the flask. An oxidant (2,6-di-tert-butyl-p-creosol ("DBPC", Fluka A.G., Germany) in the amount 0.1 to 0.2 wt % was added in the solution to avoid any potential degradation of the polyethylenes. The nominal compositions of series of blends made under this series of experiments are shown in Table-1 below.

At lower concentration of high molecular weight polyethylene, mechanical stirring was readily feasible. However, at higher concentrations the solution required that they be mildly shaken as the mechanical stirring became difficult due to the observation that solution began to climb up the rod with agitation. In such cases occasional hand shaking of the flask was done to facilitate the dissolution of polymer. After the two polymers were homogeneously mixed, the solution was poured into an aluminum tray. The solvent was let evaporate under an evacuation hood for number of days, usually for 7-10 days. After bulk of the solvent was removed, the final drying of the material was carried out in a vacuum oven (~ 70°C) for about 24-48 hours. Subsequently, the material was compression molded into thin sheets of about 1 mm in thickness @ 170-240°C with 50-150 bars of pressure. Dumbell specimens were cut from these sheets and following standard ASTM-D-638M (equivalent to DIN-53457 Iso-R-527) tensile testing method, room temperature mechanical properties were evaluated. Reported values are of the average values of 3-5 measurements of equivalent samples.

Table-1

Mechanical Properties of Blends of HDPE and UHMWPE

Example (number, #)	Nominal Composition (HDPE/UHMWPE)	Stress at Break (MPa)	Elongation at Break (%)
1*	100/0	21.5	125
2	99.9/0.1	23.2	398
3	99.8/0.2	22.7	609
4	99.5/0.5	20.7	214
5	99/1	21.4	245
6	98/2	20.3	419
7	95/5	19.8	409
8	90/10	19.7	477
9	80/20	39.4	939
10	60/40	44.2	708
11 *	0/100	52.9	536

* comparative examples

It is noted from column 3 and 4 where the tensile strength at break and elongation at break data are shown, that the blend compositions containing ultra-high molecular weight polyethylene have dramatically large elongations as compared to the pure HDPE (1) , and greater elongations than those to be expected from an average of the contributions of the HDPE and the UHMWPE (1,11). Thus, for example, example # 2 which contains only 0.1 % of the UHMWPE, exhibits elongation which is larger by a factor of at least 3 (i.e. more than 300 %) over the pure HDPE, while there is only a minor change in its tensile strength. Similarly, example # 6 when 2 % of the UHMWPE is incorporated, elongation of the HDPE increases by about 700 % with simultaneous increase in the tensile strength of HDPE by nearly 100 %.

Example 12 - For illustrative and comparison purposes, polyethylene blends incorporating long chains were also

made by melt mixing. Generally speaking, the melt mixing and processing of very high molecular weight is not readily feasible at the conventional temperatures and torques available in laboratory scale units such as Brabender extruder. However, compositions containing up to 5 wt % of the UHMWPE were found to be capable of effective mixing and thus melt mixed in a Brabender mixer at 240°C. These were subsequently extruded in the form of strip using a rectangular die of opening of 25 mm in width and 2.5 mm in thickness. A Haake model PL-2000-6 single-screw extruder with four heating zones each set nominally at 220°C was used. Dumbbell specimens from the center portion of the extruded strip were cut for tensile measurements. Results obtained from the melt mixed materials compared to those obtained from solution matched satisfactorily and were within the experimental error of typical tensile tests, i.e. within 10 %.

Examples 13 to 19 - Mechanical data evaluated for of blends of linear low density polyethylene with high molecular weight polyethylene are exemplified in Table-2. An LLDPE SLP-4-2219 sold by Exxon Chemical Co., U.S.A., was used. The SLP-4-2219 is a linear copolymer of ethylene and butene. Its weight average molecular weight was about 26,000 and Mw/Mn ~ 2.0, butene content ~ 8.7 wt % and density of about 0.91 (g/cm^3). DSC measurement provided a Tm value of about 103.4°C. Blend preparation and testing was as described for Examples 1 to 11. For this series of blends M_H/M_C was about 75.

Table-2

Mechanical Properties of Blends of LLDPE and UHMWPE

Example (number, #)	Nominal Composition (LLDPE/UHMWPE)	Stress at Break (MPa)	Elongation at Break (%)
13*	100/0	8.4	81
14	99/1	8.1	63
15	98/2	8.1	83
16	95/5	9.2	157
17	90/10	11.5	656
18	80/20	11.4	685
19	60/40	24.8	849
11*	0/100	52.9	536

* comparative examples

It is clear from the data shown in above Table-2, that compositions containing less than about 5 wt.% high molecular weight species dramatically enhanced the elongational properties of SLP-4-2219. Thus for example it is noted at 10-20 % of HMWPE that both the tensile strength (stress at break) and elongation at break increase. The former by about 30 % and the latter by more than 800 %, respectively.

Examples 20 and 21 - Mechanical data evaluated for of blends of another linear low density polyethylene with the HMWPE of Examples 13 to 20 are exemplified in Table-3. An LLDPE Exxact® 3010C sold by Exxon Chemical Co., U.S.A., was used. This LLDPE is a linear copolymer of ethylene and butene having weight average molecular weight of about 78,000 and Mw/Mn ~ 2.0, butene content ~ 14 wt % and density of about 0.90 (g/cm^3). DSC measurement provided a Tm value of about 91°C. Blend preparation and testing was as described for Examples 1 to 11. For this series of blends M_H/M_C was about 25.

Table-3

Mechanical Properties of Blends of LLDPE and UHMWPE

Example (number, #)	Nominal Composition (LLDPE/HMWPE)	Stress at Break (MPa)	Elongation at Break (%)
20*	100/0	25.1	864
21	95/5	27.5	946
11*	0/100	52.9	536

* comparative examples

Table-3 illustrates the significant enhancement of elongation when of another LLDPE-based composition contains the HMWPE as described for the invention, and as well an improved stress at break from the value to be expected from a linear contribution from the respective components.

Examples 22 and 23 - Mechanical data evaluated for a blend of a commercial low density polyethylene with the HMWPE of Examples 13 to 20 are exemplified in Table-4. LDPE-180 sold by Exxon Chemical Co., U.S.A., was used. This LDPE is a linear homopolymer of ethylene having weight average molecular weight of about 74,000, density of about 0.92 (g/cm^3), and M.I. 2.0 (190°C., 2.16 kg). DSC measurement provided a Tm value of about 108°C. Blend preparation and testing was as described for Examples 1 to 11. For this series of blends M_H/M_C was about 27.

Table-4

Mechanical Properties of Blends of LDPE and UHMWPE

Example (number, #)	Nominal Composition (LDPE/HMWPE)	Stress at Break (MPa)	Elongation at Break (%)
22*	100/0	14.2	641
23	80/20	25.8	815
11*	0/100	52.9	536

* comparative examples

Table-4 illustrates the significant enhancement of elongation when an LDPE-based composition contains the UHMWPE as described for the invention, and as well the improved stress at break (exceeding by a factor of 80% the value to be expected from a linear contribution from the respective components).

Although the invention has been described with respect to particular materials, means and embodiments it is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the appended claims.

Claims :

1. Use in a polyethylene blend composition of at least 0.1 % by weight up to but less than 40 %, based on the total composition weight, of a high weight-average molecular-weight polyethylene having a weight-average mol. wt. greater than 1.5×10^6, for the purpose of improving composition elasticity, wherein in addition to the high weight-average molecular-weight polyethylene the composition comprises from 99.9 to 60 % by weight, based on the total polymer weight, of conventional polyethylene polymers having a weight-average mol. wt. less than 1×10^5.

2. The use according to claim 1 wherein said conventional polyethylene polymers are selected from one or more of ultralow-density ("ULDPE"), very low density ("VLDPE"), low density ("LDPE"), linear low density ("LLDPE"), and high density ("HDPE") polyethylene.

3. The use according to either of claims 1 or 2 wherein said high weight-average molecular-weight polyethylene has a weight-average mol. wt. of at least 2×10^6.

4. The use according to any of the preceding claims wherein the ratio of the molecular weight of high molecular weight and conventional polyethylene ("M_H/M_C") is greater than 1.

5. A polyethylene molding composition comprising a blend of a) more than 90 wt.%, based on total weight of polymer, of one or more of conventional polyethylene polymers, and b) less than 10 wt. % of high weight-

average molecular-weight polyethylene having a weight-average mol. wt. greater than 1.5 x 10^6.

6. A polyethylene film composition comprising a blend of a) more than 85 wt.%, based on total weight of polymer, of one or more of conventional polyethylene polymers or copolymers, and b) less than 15 wt. % high weight-average molecular-weight polyethylene having a weight-average mol. wt. greater than 1.5 x 10^6.

7. The composition according to either of claim 5 or 6 wherein said conventional polyethylene polymers are selected from one or more of ultralow-density ("ULDPE"), very low density ("VLDPE"), low density ("LDPE"), linear low density ("LLDPE"), and high density ("HDPE") polyethylene.

8. The composition according to any of claims 5 - 7 wherein said b) polyethylene has a weight-average mol. wt. of at least 2 x 10^6.

9. The composition according to any of claims 5 - 8 wherein the ratio of the molecular weight of high molecular weight and conventional polyethylene ("M_H/M_C") is greater than 1.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L23/04 C08L23/06 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 273 284 (NIPPON OIL CO., LTD.) 6 July 1988 see page 2, line 6 - line 7 see page 2, line 26; claims ---	1-9
A	EP,A,0 230 750 (NIPPON OIL CO., LTD.) 5 August 1987 see page 2, line 5 - line 6; claims -----	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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